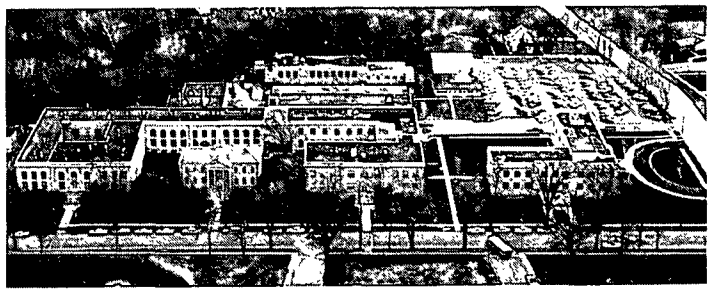

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

RAMAN MICROPROBE STUDIES OF FIBER TRANSFORMATIONS DURING PRESS DRYING

Project 3509-1

Report Two

A Progress Report

to

THE FOREST PRODUCTS LABORATORY

December 15, 1983

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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SUMMARY

The effect of press drying on the state of molecular aggregation in high-yield pulp fibers has been investigated using Raman spectroscopy and x-ray diffraction. Raman microprobe measurements on press-dried eucalyptus sheets showed areas under the knuckles of drying screens to be approximately 10% higher in cellulose k_I content than areas between the screens. Measurements on high-yield oak sheets showed those press-dried at 300°F to have higher k_I content than those dried at 160°F. X-ray diffractometric measurements on these sheets also indicated higher ordering in the sheets dried at 300°F.

The results have revealed a tendency for cellulose molecules to aggregate at a very high rate when high-yield pulp fibers are subjected to elevated temperatures in the presence of moisture. This phenomenon may be a key factor in development of the desirable properties of press-dried sheets.

It is recommended that future work focus on measurement of rate parameters for the aggregation, and on the dependence of the rates on pulp history.

BACKGROUND

The unique character of the bonding system developed in press drying was recognized in the early work of Setterholm and Benson (1). Enhanced bonding has been attributed to hemicelluloses in high-yield pulps, whereas the improved creep properties and moisture resistance have been ascribed to effects of lignin in response to conditions which promote thermoplastic flow (2) and (3).

In all of the prior studies it has been implicit that the cellulose is relatively inert and that it is not modified in the course of press drying. The SEM micrographs suggested, however, that conditions quite likely to induce polymorphic change may occur, at least under the knuckles of press drying screens. The challenge, therefore, was to establish whether such changes do occur.

The approach adopted was an extension of our earlier studies of polymorphic transformation in cellulose based on analysis of the Raman spectra (4,5,6). In order to extend our methods to analysis of press-dried material, it was necessary to use the Raman microprobe which permits acquisition of spectra from microscopic domains.

RESULTS AND DISCUSSION

EUCALYPTUS PULP

The first series of experiments was carried out on a press-dried sheet prepared at the Forest Products Laboratory from a eucalyptus pulp. SEM micrographs of the sheet are shown in Fig. 1. It is clear from the micrographs that the fiber segments in the zones under the knuckles have been deformed considerably more than fibers between the knuckles. This effect is quite similar to the observation in the SEM micrographs prepared at the Forest Products Laboratory on earlier samples of press-dried eucalyptus sheets.

Raman spectra were recorded for six domains in the press-dried sheet. Three were domains that had fallen under knuckles of the wire screens during drying. The other three were domains located between the knuckle areas. Two representative spectra are shown in Fig. 2.

Though the spectra appear quite similar, there are meaningful differences in the relative intensities of the different spectral components, particularly in the regions between 250 and 600 cm^{-1}. The differences are brought out quite clearly in the computer resolution of the spectra into the components corresponding to different standards. The results of the three computer resolutions are shown in Table I.

The three components k_I, k_{II}, and k_0, shown in Table I, correspond to the molecular conformations which are dominant, respectively, in celluloses I and II, and in amorphous cellulose. The data in the table indicate an average k_I content of 78.7% under the knuckles and an average of 69% elsewhere, indicating an average increase of 9.7% in k_I content as a result of dwell under the knuckles during the press drying.

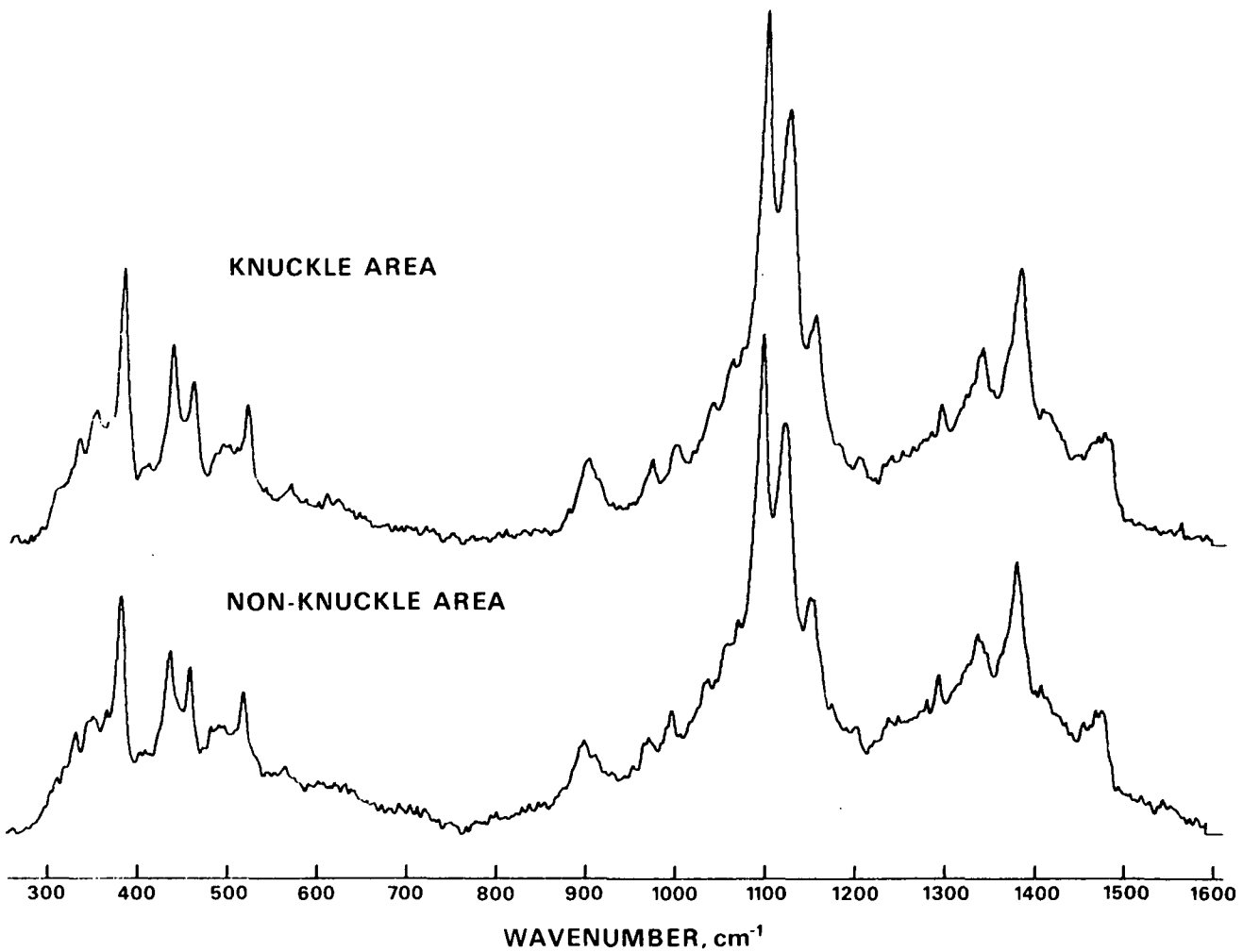

Figure 2. Raman spectra of domains approximately 40 μm in diameter, recorded with the microprobe using the 4X objective. Knuckle spectra were from domains centered in the knuckle impression. Nonknuckle spectra were centered between knuckle impressions.

The most significant implication of our observations is that the molecular mobility associated with the high temperature and moisture content during press drying can promote measurable changes in conformation and crystallinity. The observation of greater order and/or crystallinity under the knuckles represents a change that is opposite to that initially anticipated when the program was undertaken. In numerous studies we had previously observed crystallization upon exposure of pulp fibers to elevated temperatures (8,9), but the times involved had always been much longer than dwell time during press drying. We had, therefore, anticipated that the mechanical disruption of the fibers due to high pressures would be dominant. In sharp contrast, our observations indicate that the molecular mobility and the tendency to higher order and crystallinity are the dominant factors.

OAK PULPS

In an effort to clarify the role of temperature in the transformations observed, a set of handsheets press dried at different temperatures were sought. Gunderson of FPL has carried out our investigation of the effects of press-drying temperature on properties of sheets prepared from high-yield oak (10). He observed significant differences between sheets dried at 160°F and at 300°F. The duration was approximately 30 seconds. Samples of these sheets were provided. The sheets had been press dried with cotton fabric inserted between the sheets and the wire screens. Thus, the stress concentrations associated with the knuckles of wire screens were minimized.

In the absence of screen knuckles to bring about concentration of stress and heat flux, it seemed to us wiser to record macro Raman spectra from broader domains to provide representative average spectra. The Raman spectra were recorded with a cylindrical lens in the laser beam, so that the sampling

In order to provide additional independent information concerning differences in crystallinity, the x-ray diffractograms shown in Fig. 3 were recorded on the press-dried oak sheets. While the differences are not dramatic, they are significant. The width at half height for the 002 peak at 22.6° is 2.17° for the sheet dried at 160°F and 2.05° for the sheet dried at 300°F, indicating greater order in the latter. The differences in the composite peak at the 101 and $10\bar{1}$ reflections are not as readily interpreted, but are no less significant. The shape of this peak between 14 and 18° suggests some polymorphic transformation as well.

The results on the oak pulp presented in Table II and Fig. 3 clearly support the conclusion derived from the data on the eucalyptus pulp that crystallization of the cellulosic component in the fibers can occur quite readily and to a significant and measurable extent during the short intervals used in press drying. Thus, it is clear that the molecular mobility of cellulose in the cell wall, at elevated temperatures and in the presence of moisture, is sufficient to facilitate increases in crystallinity and order in the crystalline domains in the cell walls.

Perhaps more important than the suggestion of higher molecular mobility is the implication that there is a relatively high driving force toward crystallization under the conditions encountered. Such a driving force is reminiscent of the tendency to aggregation in synthetic polymers that have been cooled rapidly from a melt. It is not uncommon, in such polymers, to observe the occurrence of crystallization and ordering in a very rapid regime. Usually this regime occurs after an induction period required for nucleation. In the case of the high-yield pulp fibers, it appears that molecules of cellulose are well-aligned and ready to undergo rapid aggregation thus eliminating the need for an induction period.

TABLE II

CONFORMATIONAL DISTRIBUTIONS OF OAK PULPS UNIFORMLY PRESS DRIED AT 160°F AND 300°F

Spectrometer Scans	160°F			300°F		
	k_I, %	k_{II}, %	k_0, %	k_I, %	k_{II}, %	k_0, %
2	56	1	43	67	1	32
4	61	1	38	70	1	29
6	64	1	35	71	1	28
8	65	1	34	72	1	27
10	66	1	33	73	1	26

RECOMMENDATION FOR FUTURE WORK

Two areas are suggested for further investigation. The first is that of the rate parameters for the molecular transformations. Knowledge of these parameters would aid engineering optimization studies as well as provide additional insight concerning the nature of the transformations. The second area is that of the relation between the history of the pulp and its susceptibility to rapid transformation during press drying.

Studies of the rate parameters would focus on measuring the rates of transformation as functions of both time and temperature. Such data would be gathered on pulps which are known to respond well to press drying. The rate data would be used to determine both the order of the reaction and the activation energy.

In the second area, studies would focus on the relationship between yield level and the response to press drying. Such information would shed additional light on the molecular basis of the effect of press drying.

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